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X. *On the Effect of Heat in lessening the Affinities of the Elements of Water.*

By the Rev. Thomas Romney Robinson, D.D., M.R.I.A., &c.

Read June 14, 1847.

At the last Meeting of the British Association, Mr. Grove announced the remarkable fact that water in contact with platinum at a high temperature, is resolved into oxygen and hydrogen gases. The most obvious explanation of this is, that heat, which in general appears as the antagonist of molecular attractions, plays the same part here, and subverts the affinity of these bodies. It was, however, objected to this way of explaining the phenomenon, that it is inconsistent with the well-known effect of heat in causing these very gases to combine; and steam is not decomposed, even at the high temperature of the oxy-hydrogen blowpipe (where it is the heating agent), unless it be in contact with a solid. These objections do not seem of much weight: there are many instances where affinities are apparently called into play at one temperature, and subverted at another; that of peroxide of mercury, for instance, which is formed by exposing the metal to oxygen at 650°, and completely decomposed at 1000°. As to the necessity of a solid being present, we know far too little of the mechanism of these molecular actions to dogmatize on the subject, especially at a time when all seems tending to prove that, if these forces be not actually forms of one common power, or, to use the ideas of geometry, particular solutions of one great physical equation, they are, at least, bound together by a most intimate correlation. But we may go a little further; for since we are compelled, in the present state of our knowledge, to consider heat as a mere system of some kind of vibratory action, we are warranted to expect its action, at the common surface of two media so different as a gas and a solid, to be widely different from what it is in either separately. However, during the discussion this question suggested itself to me: if heat be, in the present instance, an antagonist of affinity, while at a lower temperature it is auxiliar to it, there must be a certain portion of the thermometric scale where its action is null, and which may be expected to present some peculiar facts that might give an insight into the theory of these attractions. This speculation might perhaps be verified by a method which I had been applying for some years during the few moments which I can spare from other pursuits. It is an application of the processes and instruments described by Mr. Wheatstone in his Memoir on determining the Constants of a Voltaic Battery (Phil. Trans. 1843), to give a measure of the affinity which combines the elements of an electrolyte, by measuring the diminution of electric intensity which its decomposition causes in the battery. It is much to be regretted that Mr. Wheatstone himself, or some other of similar acquirements, has not followed up this part of electro-chemical science; for it seems capable of giving in many instances those numerical values of affinity which are required to bring chemistry more fully within the domain of mathematical investigation. A very brief explanation of it will serve both to explain my own communication, and, I hope, to inspire in such members of the Academy as may not be acquainted with the theory on which it is based, a wish of becoming more familiar with it.

It is well known that the energy of a voltaic current is expressed by the formula

$$\mathrm{F} = \frac{\mathrm{E}}{\mathrm{R} + r},$$

in which the numerator represents the intensity of its exciting cause, and the denominator the sum of the resistances which oppose its transmission. The theoretical reasoning on which it is based is, of course, in some degree, hypothetical; but it has received most ample verification from experiment in every instance of its application. The symbol R denotes the sum of the resistances of the fluids interposed between the metals of the battery; it varies with their composition, and differs in no respect from that of metals, being like them directly as the length of the conducting medium, and inversely as its transverse section. The remaining resistances, being metallic, are represented by r; both can be expressed directly in revolutions of Mr. Wheatstone's Rheostat.

The quantity E denotes a change of electric condition produced by the chemical changes occurring in the circuit, and *strictly proportional to their inten-*

*sity.** It is therefore quite independent of the magnitude of the surfaces which are in action, as (for example) the measure of gravity at our earth's surface is independent of mass. By establishing a measure of it, we of course obtain a measure of the forces producing it when they can be assigned; and though these are in general mixed in considerable complexity, yet it is often possible to separate their values. For instance, in the common voltaic cells, if we conceive a plate of pure (or amalgamated) zinc immersed in dilute sulphuric acid, along with, but not touching, a plate of copper, no sensible action takes place, notwithstanding the existence of very energetic affinities tending to produce it, till an electric current is permitted to circulate by connecting the metals. Then the zinc is oxidized at the expense of a portion of the water present, whose equivalent hydrogen is evolved as gas. The forces which tend to favour this must be regarded as exciting the current, those which are opposed to it as antagonists or negative. We have, therefore,

+	−
1. Affinity of zinc for oxygen.	5. Affinity of hydrogen for oxygen.
2. ,, sulphuric acid for oxide of zinc.	6. ,, copper for oxygen.
	7. ,, zinc for hydrogen.
3. ,, copper for hydrogen.	8. ,, sulphuric acid for water.
4. ,, water for sulphate of zinc.	

Of these 3 is probably insensible, and 7 feeble; and it is known that 2, 4, and 8 have no appreciable effect. If, therefore, we represent the affinity of zinc for oxygen by $z.o$, &c., we have

$$\mathrm{E} = z.o - h.o - cu.o. \tag{a}$$

But if, as in Daniell's battery, instead of permitting the hydrogen to be evolved, we present to it, at the place of its evolution, a substance from which it can obtain oxygen, such as sulphate of copper, *that* change increases the intensity of the current by $ho. - cu.o$, and the total effect is

$$\mathrm{E} = z.o - 2\,cu.o. \tag{b}$$

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[*] It seems impossible to disturb the molecules of a body from their normal condition without exciting electricity; compression, friction, fracture, heat, magnetism, chemical action, vaporization, and congelation, are familiar examples: and, on the other hand, electricity can be made to reproduce several of these at pleasure.

If several cells be combined in a battery, it is also known that E and R are the sums of those quantities for each cell, even when the chemical actions in them are unequal, or in some of them antagonistic; the latter case belonging to the formula

$$\mathrm{F} = \frac{\mathrm{E} - e}{\mathrm{R} + y + r},$$

e and y being the intensity and resistance of the negative cell. Let us apply this to the common voltameter, containing water, acidulated with sulphuric acid to make it a better conductor, and provided with platinum electrodes. This cell, before it is made part of the circuit, is of course inert; but the current, decomposing the water, coats the anode, or positive platinum, with a film of oxygen retained there, either as peroxide of hydrogen, or, as seems more probable, condensed into the fluid state by the *enormous* force which capillary phenomena prove to exist at the surface of solids;* the hydrogen being similarly attached to the cathodes. These, with the platinum, act against the current with the negative intensity, $o.p + h.p - h.o$;† and unless its E be considerable, arrest it; till they are weakened by the gradual solution of the condensed gases in the electrolyte. But if the battery have sufficient power, the decomposition proceeds, till the capillary force of the electrode surfaces can no longer detain the accumulated gases, and their excess escapes, the peculiar charge of the electrodes *being still maintained.* The continued evolution of the gases adds another negative, $h.o$; and as $p.h$ is most probably insensible, the expression of this force, which I call electrolytic intensity, becomes

$$e = o.p - 2h.o. \qquad \text{(c)}$$

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* Charcoal absorbs in this way 9.25 times its bulk of oxygen. Supposing the carbon to be as dense as diamond, it would occupy about one-third of the space; were the condensed gas to fill all the remainder, its pressure must be at least fifteen atmospheres, but as it is probably in a film of evanescent thickness, the force is very much greater than even this.

† This is probably the intensity of the gas battery, but I have not access to one of these curious instruments. The quantity $o.p - h.o$ can be obtained by measuring the intensities of a combination of zinc and platinum, excited with dilute sulphuric acid, and then with that and sulphate of platinum, being their difference. If the cathode be a metal easily oxidated, its affinity is substituted for that of the condensed hydrogen, and the expression is, say for zinc,

$$e' = o.p - h.o - z.o,$$

by means of which a wide range of them may be determined.

Now it is obvious that, if this quantity be measured at the ordinary temperature of the atmosphere, and then near the boiling point of water, any difference that is found sufficiently great to be unconnected with the thermo-electric indications that sometimes arise from the dissimilarity of the electrodes, must belong to $h.o$; as the affinity of platinum for oxygen cannot be supposed to vary at such low heats. The actual experiments, however, require considerable care, and I am induced to describe them at more length than would be necessary, but for my hope that the detail may be of some use to any who may feel disposed to pursue this investigation.

The methods used to determine these quantities differ but little from those given by Mr. Wheatstone in the Memoir already referred to. The most important deviation is in the measure of intensity. He assumes it to be the number of turns of the rheostat which must be added to the circuit, in order to reduce the deflection of a rheometer from 45° to 40°. For this I have ventured to substitute another, namely, the sum of the resistances required to bring the rheometer to 45°. This is equivalent to assuming as the unit current one which produces that deflection. Supposing it attained by introducing into the circuit a resistance ρ', the fundamental equation gives

$$1 = \frac{\mathrm{E}}{\mathrm{R} + r + \rho'}; \text{ hence } \mathrm{E} = \mathrm{R} + r + \rho'.$$

Its advantages consist in giving a larger scale, and in being liable to less *absolute* errors. These errors are of two kinds: the one of observation caused by the uncertainty of reading the divisions of the rheometer, and the varying contact of the rheostat; the other arising from changes in the magnetic intensity of the needle. With respect to the first class, they are easily valued by the same application of the calculus of probabilities, which has so much advanced astronomy and other branches of physics. Comparing each observation of a series with their mean, it is possible to deduce what amount of error is as likely to affect a single observation as not. This is called the Probable Error; the value of the observation is inversely as its square, and that of the mean of the whole series as the same inversely, and also as their number directly. Now from a considerable series I find these probable errors are, with my apparatus, ± 7.7; and ± 5.1 for Mr. Wheatstone's E and mine; while the quantities themselves are 118.9 and 236.4. The *relative* accuracy is therefore as one to three. As to the second, it is easily shown that a diminution of the needle's magnetism lessens my E, and increases the other in a still greater proportion: there would be no difficulty in investigating the correction required, but it is much simpler to keep the needles in a state of saturation, which can be performed during an experiment by means of a small, flat helix, like that which Mr. Elias has described in the Philosophical Magazine for November, 1844.*

The electrolytic intensity e is easily determined on the same principles. Let ρ be the rheostat resistance which must be added to produce the same deflection as is observed with the voltameter included in the normal circuit; and ρ'' that required to give 45° along with the voltameter, we have the equations,

$$\frac{\mathrm{E}}{\mathrm{R}+r+\rho}=\frac{\mathrm{E}-e}{\mathrm{R}+r+y};\quad \frac{\mathrm{E}}{\mathrm{R}+r+\rho'}=\frac{\mathrm{E}-e}{\mathrm{R}+r+y+\rho''}=1;$$

hence

$$e=\mathrm{E}-\frac{\mathrm{E}\rho''}{\rho'-\rho},\quad y=\rho'-\rho''-e.$$

In this process, however, each result is derived from six observations; and therefore, independent of real changes, the errors of observation must have a greater effect than in E, which is given by three.

The quantity R has been determined by Mr. Wheatstone's second method. The rheostat being at zero, the first copper and last zinc are connected by a wire, whose resistance $= r$ (that of the normal circuit), plunged in two small mercury cups drilled in their connectors: the deflection being noted, the dividing wire is removed, and the entire current brought to the same resistance by the rheostat. The added resistance $=$ R. Simple as this is, some precautions are requisite to obtain uniform results. The wire is coated at its extremities with lac, so that only its transverse sections touch the mercury; it is of platinum, that it may be unchanged by use; but as this metal is easily heated by voltaic currents (which increases its resistance), it is lapped with fine thread, and kept wet with water.

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* That which I use has sixteen feet of copper wire, $\frac{1}{10}$ thick, coiled into a cylinder 3.7 diameter, and 1.2 thick, with a central aperture of 1.2 also. The needle is passed through this, having its poles connected by a bent piece of soft iron; and a current even one-fifth of that produced by one of the cells which I use, produces the maximum. It appears to me that this would be useful in magnetic expeditions.

For the same reason the coils of wire which are used to give resistances beyond the range of the rheostat, are arranged in a glass jar filled with a mixture of alcohol and water, the latter alone being rather too good a conductor. This may seem a needless refinement; but I found a set of coils which gave the resistances 1091 in air, sink to 1030 when thus managed, though the deflection was only 45°.

By the same means the constant r is obtained: calling the resistance of the dividing wire W, and adding to r the resistance a before dividing the current, we have the two equations,

$$\mathrm{R} = \frac{\rho \times \mathrm{W}}{r}; \quad \mathrm{R} = \frac{(\rho' - \alpha) \times \mathrm{W}}{r + a};$$

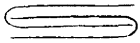
from which

$$r = \frac{\rho a}{\rho' - \rho - a};$$

and using several values of a we get a set of equations of condition from which it is found exactly. In these experiments it is 7.3.

The apparatus which I used was constructed for other researches, requiring very powerful currents, and therefore the rheometer is not very delicate. Astatic needles would soon lose their quality in it, and numerous convolutions of fine wire introduce too much resistance. It consists of a rectangle of copper bar one-fourth inch square, six inches by three, with a needle three inches long supported in its centre on a point of steel and ruby cap. The circle is divided only to degrees; but I estimate tenths of these pretty sure. I have said that I assume as the unit of current that which deflects this instrument to 45°; I may add, that this is able to afford, in five minutes, by the decomposition of water containing one-eighth of sulphuric acid, with electrodes of bright platinum, 6.57 cubic inches of gases at 60° thermometer, and 30°.0 barometer.

The rheostat is analogous to the second form of that most valuable instrument described by Mr. Wheatstone; its copper wire is one-twelfth diameter, and a revolution 8.3 inches. Though the moveable piece which connects its spiral with the circuit is kept in contact by a rather considerable weight, I find that its action is not perfectly uniform, and this, with a suspicion that even such thick wire may not be entirely secure from the effect of heat, has induced me to have one made on a different principle. In it the varying resistance is given by a platina wire, whose effective length is varied by raising it out of mercury; its imperfect conductivity permits a moderate length of it to be sufficient, and it can be kept cool as above. On a future occasion I will submit its action to the Academy; for I think it of the highest importance to make as perfect as possible these electro-chemical measurements.

The voltameter which I used has electrodes two inches by one, each folded thus, . That which is used as anode is still coated with black platinum by electric decomposition of its chloride, the other is now in its ordinary state. Particular attention must be paid to the purity of the sulphuric acid used, as a very minute portion of nitric acid or metallic sulphates will change the electrolytic intensity.

After this long preface, the experiments themselves will require little detail; it will be sufficient to give the numbers of one in full, and the results of the rest. The battery consisted of five cells, excited by chloride* of copper and hydrochloric acid. The voltameter being in circuit, the deflection was 60°.7; when removed, $\rho = 350.5$ of the rheostat was added to produce the same deflection. The voltameter, with $\rho'' = 255.9$, gave 45°; when removed, $\rho' = 899.3$ gave the same deflection.

The current being divided by the platinum wire, the deflection is 66°.0; the entire current, with 233.1, gives the same. Hence $\mathrm{R} = 233.1$ for the five cells,

$$\mathrm{E} = \mathrm{R} + r + \rho' = 1114.6\,; \quad \mathrm{E} \times \frac{\rho''}{\rho' - \rho} = 519.7\,;$$

and, in fine,

$$e = 594.9\,; \quad y = 48.5.$$

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* Prepared by dissolving the sulphate in strong hydro-chloric acid; Kane has shown that it is decomposed, and an extremely concentrated solution is thus obtained, a small quantity of which is sufficient to excite the cells for a long time, and, from the greater solubility of the chloride, the action is more uniform than with the sulphate. Its intensity is less, but its R still more so; so that the current is often more powerful. Six measures of it give

$\mathrm{E} = z.c - 2\,cu.c = 226.8\,; \quad \mathrm{R} = 50.3\,;$

Daniell's cell, ... $\mathrm{E} = z.o - 2\,cu.o = 275.1\,; \quad \mathrm{R} = 55.9\,;$

Chloride of copper; sulphuric acid, . . $\mathrm{E} = z.o - 2\,cu.c = 215.2\,; \quad \mathrm{R} = 50.6.$

It should seem from this that the affinity of zinc for chlorine is greater than for oxygen, and that this is the case also with copper, but that the difference is still greater.

As might be expected, R changes during a series of experiments, both from the chemical changes which occur and the heat which they produce: y also lessens from the heat evolved by the current. Were the zinc and acids used in the battery pure, E would not vary; but as this is not the case in actual work, the substances deposited on the metal, notwithstanding the most careful amalgamation, cause it to decline, especially when the action is maintained for several hours. Therefore each experiment must be complete in itself, and independent of the rest. This series gives

	$e = 594.9$	$y = 48.5$
	605.4	45.8
	576.6	53.6
	593.4	39.5
	585.1	42.8
	582.8	45.1
	577.6	52.7
	612.3	41.1
	606.3	49.1
	618.0	29.4
	608.6	31.8
	625.7	21.7
Mean	$e = 598.9$	$y = 41.8$. Temperature = 61°.2.

The probable error of a single $e = \pm 10.9$; for the mean ± 3.1.

The voltameter was now placed on a disc of wood in an earthen cylinder 6.5 inches diameter, and the same depth, which was filled with water, covered by a film of oil, to prevent evaporation. Steam was passed into this by a make-shift apparatus, to raise its temperature, which was measured by a thermometer in contact with the voltameter at the side opposite to the steam-tube (the electrodes preventing its being introduced into the instrument). The heat, however, was pretty uniformly diffused, in consequence of the concussions occasioned by the condensing steam. I obtained

$e = 493.3$	$y = 82.6$	T = 118°
518.7	66.2	114°.5
586.0	19.9	117°.0

e = 589.5	y = 16.4	T = 120°.0
566.9	27.0	124°.0
563.4	24.5	130°.0
567.2	27.7	130°.0
599.8	+ 1.1	134°.0
555.6	− 11.7	192°.0
585.6	+ 19.3	154°.0
570.0	28.9	148°.0
577.3	18.6	144°.0
543.9	44.0	139°.0
581.8	14.1	132°.0
Mean,[*] e = 567.6	Mean, y = 24.5	Mean, T = 135°.4

The probable error of the mean e is here = ± 5.3.

According to this, a rise of temperature, amounting to 74°.2, lessens the electrolytic intensity of water by 31.3, equivalent to 42.19 for 100°. Now, as to this effect being real, and not error of observation, I would remark that the probable error of the difference between the two values of e = ± 6.2; less than a fifth of the difference above. Therefore it can easily be computed that it is as 10,000 to 1 that the error of observation is not so great. From the equation (c) we infer that 100° lessens the affinity of hydrogen and oxygen 21.1.

I afterwards got a better steam arrangement, and obtained

e = 544.4	y = − 9.3	T = 198°
522.9	+ 40.9	200°
549.3	20.5	200°.5
532.6	26.3	200°.5
500.5	22.4	201°.5
499.4	+ 24.5	202°.0
564.6	− 16.9	202°.0
566.8	− 19.9	202°.2
574.4	− 14.5	202°.2

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[*] The last six were obtained on a different day; and this mean is deduced from the separate means, giving each its probable weight.

$e = 506.6$	$y = +10.5$	$\text{T} = 202^\circ.0$
519.2	$-$ 1.1	$202^\circ.0$
517.4	$+11.7$	$202^\circ.0$
Mean, $e = 531.0$	$y =$ 7.9*	$\text{T} = 201^\circ.2$

The probable error of the mean e here is ± 4.6; the set is more consistent, and gives the change of $e = 67.9$ for 140°, or 48.5 for 100°. The change of *h.o* is 24.2.

One only objection occurs to me against this conclusion: it may be said that heat acts merely by expanding the evolved gases, and thus facilitating their escape from the electrodes. If so a similar effect should be produced by removing the pressure of the atmosphere; and, to try this, I arranged the voltameter under the receiver of an excellent air-pump. Some difficulty was found from the rapid effervescence which occurs at the first contact, and would, without precaution, blow the fluid out of the voltameter. This was obviated by adding 700 to the circuit, removing 400, and then the rest; thus moderating the initial burst of gases. The pressure was reduced to $0^{i}.6$ before each observation, but the extrication of gas increased it to about $1^{i}.1$ before the deflection was read. The barometer = 29.55; temperature of room = 64°.6. The results are:

$e = 550.0$	$y = 114.3$†	$\text{P} = 1^{i}.1$
627.1	33.2	$1^{i}.2$
609.1	48.3	$1^{i}.2$
595.3	53.1	$1^{i}.2$
601.2	43.2	$1^{i}.2$
595.6	50.8	$1^{i}.2$
595.4	50.4	$1^{i}.2$
605.5	49.9	$1^{i}.0$
609.9	40.5	$1^{i}.2$
565.3	48.6	$1^{i}.1$
552.1	48.8	$1^{i}.1$

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* The conducting power of the water also increases with the heat; but y is, of necessity, less accurately determined than e. It almost seems as if the resistance of it would become insensible by a little elevation of temperature.

† The connecting wires were not sufficiently amalgamated. This does not, however, affect e; it was corrected immediately.

574.1 . . . . 18.7 . . . . $1^{\text{i}}.0$

Mean of 12, $e = 589.6$ . . . . $y = 50.0$ . . . . $\text{P} = 1^{\text{i}}.14$*

The probable error of the mean e is here $= \pm 4.8$, and the difference $= 9.3$. Of this I conceive 2.0 is accounted for by the 3°4 of higher temperature. The remaining 7.3 is 1.27 times the probable error of that difference ($= \pm 5.73$). The chances are, therefore, 3 : 2 that it *is* error of observation. This does not exclude the probability of some effect being produced by the freer escape of the gases; but it does establish that the affinity is *not* changed. The same may be said of the conducting power of the electrolyte. I was surprised at this result, because gas appeared under the action of a single cell, and with two its evolution seemed considerable. The deflection, however, was only 0°.1 With three the action was powerful, and the deflection = 33°.

This effect of heat on water is in singular contrast to its action on the affinity of metals, which does not change in the same circumstances. I have already stated that in Daniell's cell the expression of the intensity is $\text{E} = z.o - 2\,cu.o$. Examining this at the temperature 62°, a mean of 12 gives $\text{E} = 275.0$, $\text{R} = 45.1$; and on heating it to 162°.8, as measured by the mean of two thermometers, one in contact with the copper, the other immersed between two leaves of the zinc, the mean is $\text{E} = 277.9$, $\text{R} = 27.3$. The values of E must be considered identical, the slight difference arising from the easier diffusion of sulphate of copper in the hot liquid. The conducting power of the fluid, on the other hand, is increased considerably, and with it the power of the cell, the currents being 5.38 and 8.50. When excited with chloride of copper and hydro-chloric acid I had previously found

$\text{E} = 228.0$ . . . $\text{R} = 48.6$ . . . $\text{T} = 61°.6$

$\text{E} = 227.3$ . . . $\text{R} = 27.2$ . . . $\text{T} = 146°.1$

Either these forces are unchanged, or the affinity of zinc changes in both cases just twice as much as that of copper, which seems very unlikely.

With a cell excited by dilute sulphuric acid whose $\text{E} = z.o - cu.o - ho$, I obtained similarly

$\text{E} = 110.1$ . . . $\text{R} = 41.5$ . . . $\text{T} = 64°.3$

$\text{E} = 136.7$ . . . $\text{R} = 28.3$ . . . $\text{T} = 159°6$

hence there is a change of $h.o = 26.6$ for 95°.3, or 27.91 for 100°, a little larger than 23.2, the probable mean of the voltameter, and perhaps to be preferred to it, as obtained by means less complex. The mean of all, 25.1, may with tolerable certainty be assumed as the real value. If we might suppose this rate of decrease to be uniform, $h.o$ would vanish at $\frac{598.9}{25.1} \times 100° = 2386°$, about half way between the fusing points of gold and cast iron. Judging from my recollection of the appearance of the platinum wire, which I saw performing the decomposition of water with Mr. Gassiot's magnificent apparatus, it must actually have been near this; but I hope before long to determine the precise point of the scale by actual measurement.

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* The pressure was less while the current of 45° passed, as less gas was evolved; its mean = 1.03.

These facts, I think, show that up to 202° the affinity of the elements of water is lessened by heat; they increase the difficulty already noticed of explaining how this agent can cause the combination of those bodies; but they are, at least, consistent with the wide range of facts which show that the character of its action is essentially repulsive. They also justify a doubt whether that combination is really produced by its direct influence, or by its evolving some other agent of opposite and more powerful tendency. Nor are we without some obscure indications that such actually is the case; for Sir Humphrey Davy found, in his celebrated Researches on Flame, that hydrogen will not burn, nor a mixture of it and oxygen explode, unless acted on by a body heated *so as to emit light.* At a temperature something lower the gases combine, without a propagation of the action from one part of the mixture to another, and apparently by its successive contact with the heated surface. In the case of chlorine, light causes the explosion at low temperatures; but the repulsive forces are feeble in this gas, as is manifest from its liquefaction at a moderate pressure. At those temperatures, too, it exercises a strong absorptive action on certain rays of light, which the experiments of Brewster prove to increase as the heat is raised. The absorption of light by oxygen is, I believe, insensible in ordinary circumstances; but the analogies of chlorine and iodine authorize a belief that it may be energetic at an elevated temperature. Yet more, as heat, when it becomes latent, changes its relations to temperature for others belonging to cohesion, may not light, when it loses its visible character by absorption (or otherwise), acquire another connected with affinity? In the slower and tranquil combustion we have evidently at work that capillary force of which I have already spoken, and which, in the instance of platina sponge, is alone sufficient to overcome the elasticity of the gases. But in ordinary cases it requires the temperature to be raised before it acts; yet even then is it not probable that, if not light, some other actinic power (like that which accompanies light in the spectrum, and is revealed to us by its chemical effects in the processes of photography) is evolved by the heat, and, though invisible, determines, in conjunction with the affinity, that atomic change which transforms the three volumes of oxygen and hydrogen into two of steam? This conjecture seems to me to derive some support from the singular fact, that when a platinum wire is traversed by a current gradually increased till it produces ignition, the first gleam that appears is not red,* but of a colour which, when I first saw it, I compared to the "lavender ray" discovered by Sir John Herschel beyond the violet, though I was surprised at seeing the tint of that most refrangible ray preceding the ray which is least so. It is quite conspicuous at about 865°; and as the mode in which it makes its appearance presents nothing abrupt or discontinuous, it seems likely that it is merely a transition from invisible rays, excited at a lower temperature, to ordinary light. These are certainly mere surmises, nor would I occupy the time of the Academy with them, but that I hope some of them may prompt experimental inquiry in a direction where, at present, our ignorance is almost total. With the same view I will add to them a suggestion, which I think deserves the consideration of some of those distinguished mathematicians who adorn our Society.

The undulatory hypothesis is as decidedly connected with *radiant* heat as with light. Can it be also applied to heat when traversing bodies by conduction; and can it be brought to bear on that class of phenomena which exhibit it as becoming latent in various changes of molecular condition, and again reappearing with the definite numerical precision of a chemical equivalent? Such an attempt, if successful, would probably unlock a whole treasure of hidden knowledge; and it would scarcely be less precious were its failure to show that in these three forms of heat we have been confounding modes of energy which are essentially distinct.

ARMAGH OBSERVATORY,
June 11, 1847.

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* This fact has recently been published by Dr. Draper in a paper containing much remarkable matter, and, I may add, curiously coincident with some of my investigations, with which, of course, it was impossible for him to be acquainted. I observed it in September, 1844, while making experiments on the application of wires faintly ignited as the lines of a micrometer, which I proposed to use with Lord Rosse's telescopes for drawing nebulæ. This mode of illumination would be perfect were it not that the heated air from the wires produces a little indistinctness.